

REMARKS

By the above actions, the title and claims 1, 3-9, 11, 12, 14 and 19 have been amended and new claim 20 presented. In view of these actions and the following remarks, reconsideration of this application is requested.

The finality of the Examiner's restriction requirement and withdrawal of claims 14-19 has been noted and applicant reserves his right to amend the withdrawn method claims in conformance with any elected claim that may be allowed along with his right to petition the final restriction requirement.

Claims 1-13 have been rejected under 35 USC § 112 as being indefinite. In response thereto, the "preferably" and range-within-range limitations have been deleted and the antecedent basis problem with regard to the water/binder ratio corrected. However, as to the term "ultra fine", applicant disagrees with the Examiner's assessment that this is an indefinite relative term. To the contrary, this term has a well establish meaning in that art of cement compositions as can be seen from U.S. Patent Nos. 5,398,759 and 4,761,183 submitted herewith. Both patents show establish particle size ranges for ultra fine cement compositions (see, col. 2 of U.S. Patent 4,761,183 and col. 6 of U.S. Patent 5,398,759, which patent also uses the term "ultra fine" in line 5 of claim 1). Therefore, since the term "ultra fine" is not an indefinite relative term, but rather has a meaning that is well known in the art to which this invention is directed, applicant should be permitted to use this term its claims. If necessary, either or both of the above cited patents can be incorporated by reference into the specification at an appropriate location to provide support for use of the "ultra fine" term in the claims. On the basis of the foregoing, the rejection for indefiniteness under 35 USC § 112 should be withdrawn and such action is requested.

Claims 1, 2 & 13 have also been rejected under 35 USC § 102 as being anticipated by the Kahn patent. However, to the extent that this rejection may relate to these claims as now presented, it is inappropriate for the following reasons.

Claim 1 relates to a composite sandwich plate-shaped construction, comprising a flat tension plate 2, 9, 17, 20, a contact layer 5 and a compression layer, the contact layer comprising an epoxy-based material or a contact glue having a bonding strength similar to that of an epoxy-based material, and the compression layer (composite material 10) being an

inorganic layer at least comprising ultra fine particles, water and a binder, the contact layer being applied to the tension plate, and the compression layer being applied to said contact layer to form the sandwich composite construction. Furthermore, as described, for example, in the first full paragraph of page 22, is shown in Fig. 2 and as set forth in new claim 20, particles are partly embedded in the contact layer and partly extend out of the contact layer, the compression layer being applied over the part of the particles which extends out of the contact layer so as to enclose them within the compression layer.

The Kahn patent does not disclose a sandwich construction formed of the three layers, let alone of the type disclosed and claimed here and described above. Instead, Kahn discloses a “concrete and steel panel 20” of a traditional concrete construction having embedded reinforcement, which is coated with an epoxy in order to avoid or diminish cracks resulting from shrinkage in the concrete and in order to enhance contact between concrete and steel. However, no epoxy layer is provided between the straightening yoke 71 and the concrete.

The problem to which Kahn is a solution, see col. 1, lines. 19-32, is to provide a steel and concrete panel that approximates the characteristics of a reinforced concrete plate but which is stronger and uses less concrete and steel than prior reinforced concrete plate. On the other hand, the present invention, instead of transferring shear forces by means of studs (e.g., bolts 72 of Kahn), the entire surface, due to the characteristics of the contact layer, will be able to transfer shear forces, thereby achieving a much stronger construction due to the load being distributed over the entire surface and not only transferred at a number of points corresponding to the number of studs. See, e.g., page 3, lines 15-19. As such, without recognition of the advantages of the present invention, no reason would even exist to provide an epoxy or comparable layer between the concrete and the yoke of Kahn. Furthermore, the inclusion of ultra fine particles in the inorganic layer “will create a very dense layer which will be substantially tighter against the ingress of chlorides, CO₂ and water. These factors altogether create a longer lasting and stronger construction.” See, page 3, lines 19-21.

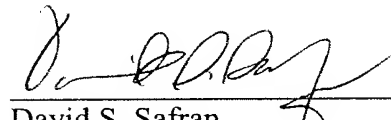
Moreover, with regard to claim 20, the use of embedded particles in the contact layer provides the further advantage of “an altogether strong and ductile construction” being created. Such a construction is clearly not disclosed or even remotely hinted at by the Kahn patent.

Accordingly, for all of the above reasons, reconsideration and withdrawal of the rejection based upon the Kahn patent is in order and is hereby requested.

As for the prior art that has been cited, but not applied against the claims, none of these references are believed to affect the patentability of the claims. Thus, no detailed comments on the unapplied prior art is considered to be warranted at this time.

Therefore, in the absence of new and more relevant prior art being discovered, this application should now be in condition for allowance and action to that effect is requested. However, while it is believed that this application should now be in condition for allowance, in the event that any issues should remain, or any new issues arise, after consideration of this response which could be addressed through discussions with the undersigned, then the Examiner is requested to contact the undersigned by telephone for the purpose of resolving any such issue and thereby facilitating prompt approval of this application.

Respectfully submitted,



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US005398759A

United States Patent [19]**Rodrigues et al.**[11] **Patent Number:** **5,398,759**[45] **Date of Patent:** **Mar. 21, 1995**[54] **SET RETARDED ULTRA FINE CEMENT COMPOSITIONS AND METHODS**[75] **Inventors:** **Klein A. Rodrigues, Duncan; Donald W. Lindsey, Marlow, both of Okla.**[73] **Assignee:** **Halliburton Company, Duncan, Okla.**[21] **Appl. No.:** **171,543**[22] **Filed:** **Dec. 21, 1993**[51] **Int. Cl.⁶** **E21B 33/13**[52] **U.S. Cl.** **166/293; 106/714; 106/808**[58] **Field of Search** **166/292, 293; 106/724, 106/728, 810, 823**[56] **References Cited****U.S. PATENT DOCUMENTS**

4,555,269	11/1985	Rao et al.	166/293 X
4,557,763	12/1985	George et al.	166/293 X
4,676,832	6/1987	Childs et al.	166/293 X
5,086,850	2/1992	Harris et al.	166/292 X
5,125,455	6/1992	Harris et al.	166/292

5,263,542 11/1993 Brothers 166/293

OTHER PUBLICATIONS

Hampel, Clifford A. et al., *Glossary of Chemical Terms* Second Edition, Van Nostrand Reinhold Company, 1982, p. 11.

Miles, "Material Safety Data Sheet", Oct. 15, 1990.

Primary Examiner—George A. Suchfield

Attorney, Agent, or Firm—Robert A. Kent

[57] **ABSTRACT**

Set retarded ultra fine cement compositions which remain pumpable for a predictable period of time at temperatures up to about 400° F. are provided. The compositions are basically comprised of an ultra fine hydraulic cement, sufficient water to form a pumpable slurry and a set retarder comprised of a water soluble aliphatic compound containing at least three carbon atoms and at least one phosphonic acid or phosphonate group.

8 Claims, No Drawings

SET RETARDED ULTRA FINE CEMENT COMPOSITIONS AND METHODS

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates generally to cement compositions utilized in the completion and repair of wells, and more particularly, to set retarded ultra fine cement compositions and methods of their use.

2. Description of the Prior Art

In cementing operations such as those carried out in completing and repairing oil, gas and water wells, a hydraulic cement composition is prepared by mixing a hydraulic cement with water and other additives, the composition is placed into a subterranean zone to be cemented and allowed to set therein into a hard substantially impermeable mass.

In the operation of wells used in the recovery of fluids from or the introduction of fluids into subterranean formations problems relating to the unwanted passage of fluids and/or fine solids into or from undesirable locations in the formation or wellbore sometimes occur. This unwanted passage of fluids and/or fine solids can severely disrupt or terminate the desired operation of a well.

The problems involving the unwanted passage of fluids referred to above, ordinarily involve the movement of fluids, such as oil, gas or water through very small undesirable openings. These problems are not unique and the solutions have traditionally involved apparatus, methods and compositions adapted to cover, seal or to otherwise plug the openings to thereby terminate the unwanted passage of fluid through the openings. The openings referred to above include: holes or cracks in well casing; spaces such as holes, cracks, voids or channels in the cement sheath deposited in the annular space between the formation face and well casing; very small spaces—called microannuli—between the cement sheath referred to above, and the exterior surface of the well casing or formation; and permeable spaces in gravel packs and formations.

It is clear that holes or cracks in well casing and/or cement sheath can permit the unwanted and therefore uncontrolled passage of fluids therethrough. Sometimes, of course, holes are deliberately made in casing and sheath by a known process called perforating in order to permit the controlled recovery of fluid from a formation or to permit the controlled introduction of fluid into a formation. The sealing or plugging of such holes or cracks, whether or not made deliberately, has been conducted by attempts to place or otherwise force a substance into the hole or crack and permitting it to remain therein to thereby plug the opening. Naturally, the substance will not plug the opening if it will not enter the opening. If the substance does not fit then, at best, a bridge, patch, or skin may be formed over the opening to produce, perhaps, a temporary termination of the unwanted fluid flow.

Substances used in methods to terminate the unwanted passage of fluids through holes or cracks in casing and/or sheath have been compositions comprised of hydraulic cement, wherein the methods employ hydraulic pressure to force a water slurry of the cement into the cracks and holes wherein the cement is permitted to harden. These methods are variously referred to in the art as squeeze cementing, squeezing or as squeeze jobs. The success of squeezing hydraulic

cement into such holes and cracks is, among other factors, a function of the size of the hole relative to the particle size of the cement as well as the properties of the slurry. As mentioned earlier, if the particle size of the cement is greater than the crack width, the cement will not enter and at best a patch instead of a plug is the result. A problem therefore is to substantially reduce cement particle size without reducing the hardening and strength characteristics of hydraulic cement.

During the construction of a well it is known to place a volume of a water slurry of a hydraulic cement into the annular space between the walls of the wellbore and the exterior of the casing wherein the cement is permitted to solidify to thereby form an annular sheath of hardened cement. The objective of the sheath, the construction of which is referred to as primary cementing, includes physical support and positioning of the casing in the borehole and prevention of unwanted fluid (liquid and gas) migration between various formations penetrated by the wellbore. If, for some reason, the hardened sheath contains spaces such as voids, cracks or channels due to problems involved in the placement of the slurry it is clear that the sheath may not be capable of providing the desired objectives. Accordingly, by employing known techniques to locate the voids, channels or cracks, a perforation penetrating the spaces can be made in the casing and sheath and cement then squeezed into the spaces via the perforation so as to place the sheath in a more desirable condition for protecting and supporting the casing and providing fluid flow control. As mentioned earlier, the success of the squeeze job is at least a function of the size of the space or spaces to be filled relative to the particle size of the cement.

Another problem incidental to the formation of the cement sheath revolves about the occasional failure of the sheath to tightly bond to the exterior wall of the casing or the interior of the borehole. This failure can produce a very thin annular space called a microannulus between the exterior wall of the casing and the sheath or the sheath and the borehole. For the reasons already discussed, it is important to place a substance, such as a hydraulic cement, in the microannulus to enable the sheath to fully provide the intended benefits. Again, as stated above, the success of squeezing cement into a microannulus space is dependent upon the relative size of the space and the particle size of the cement.

The solid portions of some producing formations are not sufficiently stable and therefore tend to break down into small pieces under the influence of the pressure difference between the formation and the wellbore. When fluid, such as oil or water, flows under the influence of the pressure difference from the formation to the wellbore the small pieces referred to above can be carried with the fluid into the wellbore. Over a period of time, these pieces can build up and eventually damage the well and associated equipment and terminate production. The art has solved this problem by placing in the wellbore a production aid which is referred to in the art as a gravel pack. A gravel pack is usually comprised of a mass of sand within the interior of a well. The sand bed completely surrounds a length of tubular goods containing very narrow slots or small holes; such goods are sometimes referred to as slotted liners or sand screens. The slots or holes permit the flow of fluid therethrough but are too narrow to permit the passage of the sand. The slotted liner or sand screen can be

connected through a packer situated up-hole of the gravel pack to production tubing extended from the wellhead. The gravel pack ordinarily consists of siliceous material having sand grains in the range of from about 10 to about 100 mesh.

The gravel pack, which can be situated in the casing in the perforated interval, traps the small pieces of formation material, for convenience herein referred to as formation fines or sand, which flows from the formation with the fluid through the perforations and into the gravel pack. Accordingly, neither formation sand nor gravel pack sand penetrates the slotted tubing and only fluid is permitted to pass into the tubular goods.

The above expedient performs nicely until undesired fluid begins to penetrate the gravel pack from the formation. At that point the flow of undesired fluid, such as water, must be terminated preferably in a way which will not necessitate removal of the gravel pack.

The problems referred to above uniformly deal with the unwanted passage of materials into or from very small undesirable openings in a well, including the cement sheath constructed during a primary cementing procedure. Still another problem involved in the construction and repair of wells involves the primary cementing procedure itself.

Primary cementing, as described above, is conducted during the construction of a well and involves the placement of a volume of a slurry of a hydraulic cement and water into the annular space between the walls of the wellbore and the exterior of primary casing such as conductor pipe, surface casing, and intermediate and production strings. The slurry is permitted to solidify in the annulus to form a sheath of hardened cement, the purpose of which is to provide physical support and positioning of the casing in the wellbore and to isolate various formations penetrated by the wellbore one from another.

A problem encountered during primary cementing is centered upon the weight (that is the density) of the slurry itself. In certain circumstances the hydrostatic pressure developed by a column of slurry overcomes the resistance offered by a formation in which case the formation fractures or otherwise breaks down with the result that a portion of the slurry enters the formation and the desired sheath is not formed. The formation breakdown thus occurs prior in time to development of sufficient rigidity or hardening of the cement to enable it to be self-supporting.

One solution has been to reduce the density of the slurry so that the pressure developed by the required slurry height will not exceed the ability of the formation to resist breakdown. This expedient can result in sheaths having physical deficiencies such as reduced strength or increased permeability or both. Another solution has been to reduce the weight of the slurry while maintaining density by reducing the quantity of slurry pumped in a single lift or stage to thus reduce the height of slurry. This expedient requires several separate stages in order to produce the required sheath length. Time must pass between stages in order to permit previous stages to develop strength sufficient to support the weight of succeeding stages. The time expended waiting on cement to set is lost time in the process of constructing the well.

Still another problem involved in the operation of wells revolves about the unwanted movement of water via cracks and fractures in the subterranean formation, whether naturally occurring or deliberately produced,

from the formation into the wellbore. Terminating this water movement may require remedial efforts other than those referred to previously which feature plugging perforations, holes, cracks and the like in casing, cement sheath and gravel packs, all of which occur within the confines of the wellbore itself.

Recently, a better solution to all of the problems mentioned above has been developed and utilized successfully. The solution involves the use of ultra fine hydraulic cement compositions and is described in detail, for example, in U.S. Pat. No. 5,086,850 issued on Feb. 11, 1992 to Harris, et al. The ultra fine cement compositions and methods described in U.S. Pat. No. 5,086,850 have been utilized successfully in primary cementing, squeeze cementing and the other forms of well cementing mentioned. However, a problem which has persisted in the use of ultra fine cement compositions occurs when the compositions are subjected to high temperatures, i.e., temperatures in the general range of from about 140° F. to about 250° F. In carrying out cementing operations of the type described above in deep hot wells, the ultra fine cement composition is heated to temperatures in the above mentioned range which, heretofore, has often caused premature gelling of the cement composition and the very severe problems attendant thereto. While prior art set retarders have been included in the ultra fine cement compositions, e.g., lignosulfonates, predictable retardation of the compositions at temperatures above about 140° F. has not been obtained.

Brothers, in U.S. Pat. No. 5,263,542, addressed the problems attendant upon the use of ultra fine cement compositions at temperatures above 140° F. and up to about 245° F. Brothers thus discloses the use of a set retarder comprised of a methylenephosphonic acid derivative.

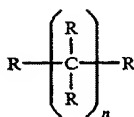
In spite of the contribution of Brothers, there remains a need for a set retarded ultra fine cement composition which remains pumpable for a predictable period of time and for methods of using such composition in remedial cementing and primary cementing operations.

SUMMARY OF THE INVENTION

By the present invention, there is provided a method of retarding the set of a slurry of an ultra fine cement in water at temperatures in the range of from about 140° F. to about 400° F. comprising adding to the slurry, as a set retarding additive, a water soluble aliphatic compound containing at least three carbon atoms and at least one phosphonic acid or phosphonate group. There is also provided by this invention a set retarded ultra fine cement composition which remains pumpable for a predictable period of time at temperatures in the range of from about 140° F. to about 400° F. and methods of using such compositions in primary and secondary well cementing operations. The set retarded composition of this invention is comprised of an ultra fine hydraulic cement having a particle size no greater than about 30 microns and a Blaine Fineness no less than about 6000 square centimeters per gram, sufficient water to form a pumpable slurry and the set retarder of this invention present in the slurry in an amount in the range of from about 0.01 pound to about 5.0 pounds per 100 pounds of dry cement therein. The set retarder of this invention is a water soluble aliphatic compound containing at least 3 carbon atoms and at least one functional group selected from the groups consisting of phosphonic acid groups, phosphonate groups, carboxylic acid groups, carboxyl-

ate groups and mixtures thereof wherein at least one of said functional groups is a phosphonic acid group or a phosphonate group.

Compounds within the scope of the above definition preferred for use herein are further defined by the formula:

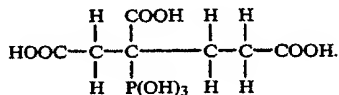


wherein R is —H,



or —P(OX)₃, X is —H, Na or K and n is 3, 4, 5, or 6 and wherein at least one of said R groups is —P(OX)₃.

The compound most preferred for use herein is the partially neutralized sodium salt of the compound 2-phosphono-1,2,4 butanetricarboxylic acid, a 25 weight percent aqueous solution, having a pH of about 2.4, the formula of which is



It is, therefore, a general object of the present invention to provide set retarded ultra fine cement compositions and methods.

Other objects, features and advantages of the present invention will be readily apparent to those skilled in the art upon a reading of the description of preferred embodiments which follows.

DESCRIPTION OF PREFERRED EMBODIMENTS

The set retarded ultra fine cement compositions of this invention remain pumpable for a predictable period of time at 25 temperatures above about 140° F. and up to about 400° F. whereby the cement compositions can be pumped into a zone to be treated without fear of premature gelation occurring. It is understood by those skilled in the art, that when a cement composition develops gel strength prior to being placed, the composition can become unpumpable and can set in undesirable locations such as in the wellbore, in conduits disposed in the wellbore or in surface pipe and equipment.

The term "gelation," when used in connection with a cement slurry, is a reference to the development by the slurry of viscosity without concurrent development of compressive strength. Ordinary development of viscosity by a cement slurry to the extent that the slurry cannot be pumped is referred to herein as "thickening time" or as "pumping time" and is defined as the time required for a slurry to develop 70 Bearden Units of consistency, or 70 Bc units, after the slurry is made. (See API Specification 10, 3rd Edition, Jul. 1, 1986 at Section 8)

A cement slurry considered herein to be useful in performing oil well cementing operations, among other things, has a pumping time in the range of from about 2 to about 6 hours depending upon temperature. Accordingly, a slurry which becomes unpumpable due to vis-

cosity increase in a period of time less than about 2 hours, or less than expected, as based upon previous laboratory testing, is said to have experienced premature gelation. The ultra fine cement compositions of this invention do not experience premature gelation.

The compositions of this invention are comprised of ultra fine hydraulic cement, sufficient water to form a pumpable slurry and a set retarder which causes the composition to remain pumpable for a predetermined period of time before gelation and setting of the composition occurs.

The ultra fine hydraulic cement is comprised of particles of cementitious material having diameters no larger than about 30 microns, preferably no larger than about 17 microns, and still more preferably no larger than about 11 microns. The distribution of various sized particles within the cementitious material, i.e., the particle size distribution, features 90 percent of them having a diameter not greater than about 25 microns, preferably about 10 microns and still more preferably about 7 microns, 50 percent having a diameter not greater than about 10 microns, preferably about 6 microns and still more preferably about 4 microns and 20 percent of the particles having a diameter not greater than about 5 microns, preferably about 3 microns and still more preferably about 2 microns.

The particle size of hydraulic cement can also be indirectly expressed in terms of the surface area per unit weight of a given sample of material. This value, sometimes referred to as Blaine Fineness or as specific surface area, can be expressed in units of square centimeters per gram (cm²/gram), and is an indication of the ability of a cementitious material to chemically interact with other materials. Reactivity is believed to increase with increase in Blaine Fineness. The Blaine Fineness of the hydraulic cement used in the cementing methods of this invention is no less than about 6000 cm²/gram. The value is preferably greater than about 7000, more preferably about 10,000, and still more preferably greater than about 13,000 cm²/gram.

Cementitious materials of particle size and fineness as set out above are disclosed in various prior U.S. Patents including U.S. Pat. No. 4,761,183 to Clark, which is drawn to slag, as defined herein, and mixtures thereof with Portland cement, and U.S. Pat. No. 4,160,674 to Sawyer, which is drawn to Portland cement. The cementitious materials preferred for use in this invention are Portland cement and combinations thereof with slag wherein the quantity of Portland cement included in any mixture of Portland cement and slag used can be as low as 10 percent but is preferably no less than about 40 percent, more preferably about 60 percent, still more preferably about 80 percent and most preferably 100% Portland cement by weight of mixture.

Some of the problems solved by the use of a cementitious material of very small particle size are attributable to the ability of the material to pass through very narrow openings and penetrate into low permeability gravel packs and formations. To solve other problems described above, the material when slurried in water must exhibit a sufficiently low slurry density to enable use in situations requiring a light-weight cement which nevertheless develops satisfactory compressive strength. In this regard the large surface area of the cement, i.e., the Blaine Fineness, renders it more reactive than cements of lower Blaine Fineness; accordingly, quantities of water greater than quantities usually

employed in well cementing operations can be employed to thereby enable the formulation of slurries of low density and low viscosity without unsatisfactory loss in strength.

Thus, slurries useful herein can be formulated utilizing ratios of the weight of water per unit weight of cementitious material in the range of from about 0.5 to about 5.0, preferably from about 1.0 to about 1.75 and still more preferably from about 1.0 to about 1.5 pounds water per pound of cementitious material. Water to cement ratios in excess of about 1.75 and up to about 5.0 can be formulated for highly specialized applications requiring slurries of very low density and very low viscosity. It is noted, however, that slurries having such high water ratios tend to exhibit free water separation and excessive solids settling. Additives can be utilized to control free water separation and solids settling.

The slurry densities of the fine cements of this invention are lower than cements having usual particle sizes because of the high water ratios required to wet all of the surface area of the fine cement. The compressive strengths, however, of the set lower density slurries are satisfactory for both primary cementing and remedial cementing purposes especially in view of the greater reactivity of the fine cements. Also, and particularly in the case of slurries formulated at high water ratios, where penetration into very small holes, cracks and openings is the goal, water may indeed be eventually forced out of the fine penetrating particles to thereby deposit in the target crack, opening or porosity a dense, high-strength and highly water impermeable mass of set cement.

Considering the range of water-to-cement ratios disclosed above, the densities of slurries which can be formulated utilizing the fine cement of this invention are in the range from about 9.4 to about 14.9, preferably from about 11.0 to about 12.5 and still more preferably in the range of from about 11.5 to 12.5 pounds per gallon of slurry.

One particular advantage, in addition to the low slurry densities available herein, is that the high water ratios produce low heats of hydration. Thus, the fine particle size hydraulic cement of this invention is quite useful when conducting cementing operations, and particularly primary cementing operations, adjacent to structures which may undergo undesired physical breakdown in the presence of produced heat. Examples of such structures include permafrost and gas hydrate zones.

Still another particular advantage accruing from using the ultra fine particle size Portland cement of this invention is the observed unexpected expansion of the cement during setting. This expansion property can help prevent the formation of microannuli when the cement is used in primary cementing operations and can help the formation of very tightly fitting plugs when the cement is used in squeeze cementing.

It is believed that this desirable expansive feature of the fine particle size Portland cement is due to the chemical content thereof and particularly to the high concentration of crystalline tricalcium aluminate (C_3A) and sulfates present therein. It is thought that a Portland cement having a maximum particle size of about 11 microns, a Blaine Fineness of preferably greater than about 10,000 $cm^2/gram$, a C_3A crystalline content of preferably about 3.0 percent or more and a sulfate content of preferably about 1.0 percent or more will exhibit

expansive characteristics desirable in an oil field cement.

Slurries of water and the fine particle size cement of this invention, as previously mentioned, are very useful to penetrate, fill and harden in fine holes, cracks and spaces such as might be expected to be found in well casing, cement sheaths, gravel packs and subterranean formations in the vicinity of a wellbore. By way of example, it is believed that such slurries are useful to penetrate subterranean formations having effective permeabilities as low as about 3000 to about 5000 millidarcies. Accordingly, a condition known as water coning, in which water from a subterranean formation enters the wellbore in a rising or coning fashion, can be terminated by squeezing a slurry of fine particle size cement of this invention into formations producing such water, wherein the formations to be penetrated can have effective permeabilities as low as 3000 to 5000 millidarcies.

In addition, a water slurry of the fine particle size cement of this invention can be utilized to terminate the unwanted flow of water through a zone in a gravel pack. In this regard such a slurry can be formulated to permeate and set in a gravel pack consisting of a packed sand bed wherein the sand in the pack has a particle size as low as 100 mesh (about 150 micron). Such a procedure can be utilized to plug channels in gravel packs created by flowing steam as well as by flowing water.

Still further, a water slurry of the fine particle size cement of this invention can be formulated to penetrate, plug and set in fine cracks in well pipe and in channels and microannulus spaces in and around the cement sheath wherein such fine cracks can be as narrow as about 0.05 millimeters (0.002 inches).

With regard to the above uses, but without being bound by the following slurry design aid, it is considered for commercial design purposes that a particle of given size in a suitable slurry as described herein can penetrate, fill and set in a crack, hole or void having a size of approximately 5 times greater than the size of the particle. Thus the 0.05 millimeter (50 micron) crack referred to above can be penetrated by a slurry of particles having a size of about 10 microns which is within the scope of the cement of this invention.

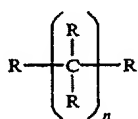
It was mentioned previously that the rate of hardening of the fine cement of this invention is related to the Blaine Fineness wherein the hardening rate increases as Blaine Fineness increases. In addition, the hardening rate is also related to the specific cementitious material being used and the temperature of the environment wherein the hardening reaction is proceeding. Thus fine particle size Portland cement, as hereinafter defined, hardens more rapidly in low temperature environments in the range of from about 30° F. to about 100° F. than does fine particle size slag cement, hereinafter defined. Also Portland cement hardens more rapidly at elevated temperatures than does slag cement.

When an ultra fine hydraulic cement slurry is used in well applications wherein the slurry is heated to temperatures in the range of from about 140° F. and higher, the cement slurry has been subject to flash gelation whereby the time that the slurry remains pumpable has been unpredictable. Even when an ultra fine cement slurry includes heretofore utilized set retarders such as lignosulfonates and other known retarders, premature gelation and setting has occurred.

As previously mentioned, Brothers, in U.S. Pat. No. 5,263,542, provided a set retarder comprised of a methylenephosphonic acid derivative in an attempt to

solve the problem of premature gelation and to extend the set time of ultra fine cement at temperatures greater than 140° F. and up to about 250° F. These problems are again addressed and solved in accordance with the present invention by including in the ultra fine cement composition a set retarder comprised of a water soluble aliphatic compound containing at least 3 carbon atoms and at least one functional group selected from the groups consisting of phosphonic acid groups, phosphonate groups, carboxylic acid groups, carboxylate groups and mixtures thereof wherein at least one of said functional groups is a phosphonic acid group or a phosphonate group.

Compounds within the scope of the above definition preferred for use herein are further defined by the formula:

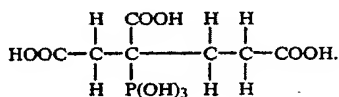


wherein R is —H,



or —P(OX)₃, X is —H, Na or K and n is 3, 4, 5, or 6 and further wherein at least one of said R groups is —P(OX)₃.

The compound most preferred for use herein is the partially neutralized sodium salt of the compound 2-phosphono-1,2,4 butanetricarboxylic acid, a 25 weight percent aqueous solution, having a pH of about 2.4, the formula of which is



The acid form of the above mentioned preferred compound is commercially available from Miles, Inc. under the tradename "BAYHIBIT-AM" in a 50 percent by weight aqueous solution. A sodium salt is also available from Miles in powder form, a one percent aqueous solution of which has a pH of about 8.5. The preferred compound is made by neutralizing a 50 weight percent aqueous solution of the acid form with sodium hydroxide and diluting to a 25 weight percent aqueous solution having a pH of 2.4.

Depending upon the particular amount of the retarder included in the ultra fine cement slurry, the slurry remains pumpable for a predetermined period of time. Generally, the set retarder is included in the slurry in an amount in the range of from about 0.01 pound to about 5 pounds per 100 pounds of dry cement in the slurry. As has been the practice in the art, prior to the preparation and pumping of an ultra fine cement slurry including the set retarder of this invention, the particular amount of retarder to be included in the slurry for a desired pumping time can be pre-determined by testing.

Particularly suitable retarders falling within the definition set forth in formula (1) above include

2-phosphono-1,4 butane dicarboxylic acid,
2-phosphono-1,2 butane dicarboxylic acid,
2-phosphono-1,2,4 pentane tricarboxylic acid,
2-phosphono-1,2 pentane dicarboxylic acid,
2-phosphono-1,4 pentane dicarboxylic acid,
3-phosphono-1,5 pentane dicarboxylic acid and
3-phosphono-1,2 pentane dicarboxylic acid.

The set retarder useful herein is preferably employed in the salt form as an aqueous solution having a pH in the range of from about 2 to about 7. It is believed that the retarder can be transported as a non-hazardous material at a pH greater than 2.

The set retarder of this invention does not cause large changes in pumping time of a slurry as a result of relatively small changes in the amount of retarder used in a slurry. That is, it is not concentration sensitive. Accordingly, use of the retarder in a cementing operation under field conditions is not complicated by the need to perform extremely precise measuring operations in order to avoid either unexpectedly low or high pumping times. Thus, good retardation control is provided by this invention.

The set retarder of this invention, in laboratory tests, has exhibited pumping time results which are reproducible within acceptable limits. Set cement which included the set retarder in the slurry exhibits satisfactory compressive strength. Test results also indicate the presence of a substantially linear relationship between the concentration of set retarder employed in a slurry and pumping time.

The above described preferred set retarders are preferably included in an ultra fine cement slurry in an amount in the range of from about 0.1 to about 2 and most preferably in an amount in the range of from about 0.3 to about 1 pound per 100 pounds of dry cement.

In addition to the set retarder as described above, the ultra fine cement compositions of the present invention preferably includes a dispersing agent to facilitate the dispersion of individual ultra fine cement particles in water and to help prevent the formation of large agglomerated particles or lumping.

While a variety of dispersing agents can be used, a particularly suitable dispersing agent is a polymer prepared by the caustic-catalyzed condensation of formaldehyde with acetone or a substance derived from acetone wherein the polymer contains sodium sulfonate groups. Such a dispersing agent is commercially available from the Halliburton Company of Duncan, Okla., under the trade designation "CFR-3 TM" dispersing agent, and is described in detail in U.S. Pat. No. 4,557,763 issued on Dec. 10, 1985 to George et al. The dispersing agent is generally added to the water utilized to form the ultra fine cement slurry whereby it is present in the slurry in an amount in the range of from about 0.5% to about 2.0% by weight of dry cement therein.

Another cement composition additive which is preferably included in the ultra fine cement compositions of this invention is a fluid loss control additive. A variety of such additives are available and can be used. A particularly preferred such additive is comprised of a copolymer of N,N-dimethylacrylamide and 2-acrylamido, 2-methyl propane sulfonic acid. The copolymer is commercially available from the Halliburton Company under the trade designation "HALAD TM -344" additive and is also described in U.S. Pat. No. 4,557,763. The copolymer is combined with an ultra fine cement com-

position in an amount in the range of from about 0.5% to about 2.0% by weight of dry cement therein.

Another preferred fluid loss control agent which can be used is a graft polymer comprised of a backbone of lignin or lignite having grafted thereto pendant groups comprising at least one of homopolymers, copolymers and terpolymers of 2-acrylamido-2-methylpropanesulfonic acid, acrylonitrile, N,N-dimethylacrylamide and their salts. Such a graft polymer fluid loss control agent is available from the Halliburton Company of Duncan, Okla., under the trade designation "HALAD®-413", and is described in U.S. Pat. No. 4,703,801 issued Nov. 3, 1987 to Fry et al. When used, the graft polymer is combined with an ultra fine cement composition in an amount in the range of from about 0.5% to about 2.0% by weight of dry cement.

Other commonly used additives in well cement compositions may also be utilized in the compositions of this invention including additives for reducing the density of the compositions such as nitrogen, perlite, fly ash, silica fume, microspheres and the like.

Also, in order to help prevent the loss of compressive strength of said cement over time, a condition referred to as compressive strength retrogression, silica flour can be included in the compositions. Generally, if silica flour is utilized it is added to the compositions of this invention in amounts in the range of from about 0.15 to about 1.0 pound of silica flour per pound of hydraulic cement used.

One preferred silica flour additive to help prevent compressive strength retrogression is available from Halliburton Company under the trademark "MICROSAND" silica flour, a high purity crystalline silica ground to a uniform particle size distribution. The average particle size of "MICROSAND" additive is 5 microns which renders it very useful with ultra fine cement. The preferred quantity of silica flour, such as "MICROSAND" silica flour, is an amount in the range of from about 0.2 pounds to about 0.8 pounds and preferably about 0.4 pounds per pound of dry cement.

As will be understood by those skilled in the art, a variety of other uses in the drilling, completion and production of wells not specifically mentioned herein can be made of the set retarded ultra fine cement compositions of this invention.

A particularly preferred set retarded ultra fine cement composition which remains pumpable for a predictable period of time at temperatures up to about 400° F. and higher is comprised of the following components:

- (a) an ultra fine hydraulic cement having a particle size no greater than about 30 microns, a Blaine Fineness no less than about 6000 square centimeters per gram, 90 percent of the particles having a diameter no greater than about 25 microns, 50 percent of the particles having a diameter no greater than about 10 microns and 20 percent of the particles having a diameter no greater than about 6 microns;
- (b) sufficient water to form a pumpable slurry (normally an amount in the range of from about 0.5 to about 5.0 pounds of water per pound of dry cement used);
- (c) the set retarder of this invention present in the slurry in an amount in the range of from about 0.01 pounds to about 5.0 pounds per 100 pounds of dry cement therein;
- (d) a dispersing agent comprised of a polymer prepared by the caustic-catalyzed condensation of

formaldehyde with acetone or a substance derived from acetone wherein the polymer contains sodium sulfonate groups present in the slurry in an amount in the range of from about 0.5 pounds to about 2.0 pounds per 100 pounds of dry cement therein; and (e) a fluid loss control agent comprised of a copolymer of N,N-dimethylacrylamide and 2-acrylamido, 2-methyl propane sulfonic acid present in the slurry in an amount in the range of from about 0.5 pounds to about 2.0 pounds per 100 pounds of dry cement therein.

The methods of this invention for cementing a subterranean zone penetrated by a wellbore at a temperature in the range of from about 140° F. to about 400° F. comprise the steps of pumping a set retarded ultra fine cement composition of this invention into the subterranean zone, and then allowing the cement composition to set into a hard substantially impermeable mass in the zone.

In order to further illustrate the compositions and methods of this invention, the following examples are given.

In the examples set out below: The hydraulic cement employed was an ultra fine cement, as previously described, having a Blaine Fineness of about 13,000 cm²/gram and an average particle size of about 3.2 microns wherein the largest particle size was not greater than about 15 microns.

The water employed to produce the cement slurries tested was deionized water.

A cement set time retarder was employed in the majority of the tests. Tests performed without a retarder are provided for comparison purposes. In some tests the cement retarder employed was a prior art retarder described in U.S. Pat. No. 5,263,542, specifically aminotri(methylenephosphonic acid). This prior art retarder is referred to in the examples as MMCR. In some of the tests a retarder of this invention, 2-phosphono-1,2,4-butanetricarboxylic acid or the sodium salt thereof, was employed. The pH of the acid form, identified as PBTC, in a 50 weight percent aqueous solution was less than 1.0. The pH of a 1% aqueous solution of the powdered sodium salt was 8.5 and is identified as SPBTC1. The pH of the partially neutralized sodium salt form, identified as SPBTC2, in a 25 weight percent aqueous solution, was about 2.4.

A dispersing agent was employed in some of the compositions tested. The dispersant was a polymer prepared by the caustic-catalyzed condensation of formaldehyde with a substance derived from acetone wherein the polymer contains sodium sulfonate groups. The dispersant is available from Halliburton Company as "CFR-3" dispensing agent and is described in U.S. Pat. No. 4,557,763.

"MICROSAND" additive, discussed above, to prevent the loss of compressive strength of set cement at high temperature, was added to the slurries tested.

The various compositions tested are set out in Tables I, II-A and IV-A, below.

EXAMPLE 1

Ultra fine cement compositions were prepared and tested for thickening time at a temperature of 187° F. The recipes of the compositions tested and the test results are set out in Table I, below.

Some of the compositions included the acid form of the retarder (PBTC) and some included the salt form

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(SPBTC1). Also, some of the compositions included a dispersant and some did not.

It should be noted that all concentrations noted in Table I refer to the specific ingredient in the undiluted (100% active) form even though the ingredient, for convenience, may have been added in a diluted form.

It is further noted that the retarder salt (SPBTC1) referred to in Table I was produced from a powder, a 1 weight percent aqueous solution of which having a pH of about 8.5.

Referring now to Table I, it is seen that thickening time can be substantially linearly increased by increasing the concentration of retarder in the slurry regardless of the form of the retarder, or the water ratio or the presence or absence of dispersant. It should also be noted that desirable pumping times were obtainable at the test temperature at various water ratios, retarder form and concentration and dispersant content.

Specifically, comparing the results obtained on compositions 1, 2, and 3, with those obtained on compositions 4, 5, and 6, reveals that the dispersant apparently has a retardant effect in combination with the retarder. Similar observations are evident when comparing compositions 7, 8, and 9, with compositions 10, 12, and 13.

Comparing the results obtained on compositions 9, 13, and 15 indicates that the salt form of the retarder, at least with respect to the salt form used in Table I, has a lesser retarding effect than the acid form.

TABLE I

Ultra Fine Cement Compositions and Thickening Times					
Composition	Water lb/100 lb dry cement	Retarder lb/100 lb dry cement		Dispersant lb/100 lb dry cement	Thickening Time @ 187° F., Hours
		PBTC	SPBTC1		
1	99.96	0.5	0	0	2.57
2	99.96	0.6	0	0	2.33
3	99.96	0.75	0	0	5.17
4	99.96	0.5	0	1.0	3.45
5	99.96	0.6	0	1.0	5.03
6	99.96	0.75	0	1.0	9.12
7	174.93	0.3	0	0	1.9
8	174.93	0.4	0	0	4.2
9	174.93	0.5	0	0	8.73
10	174.93	0.3	0	1.0	3.7
11	174.93	0.35	0	1.0	5.4
12	174.93	0.4	0	1.0	7.3
13	174.93	0.5	0	1.0	12.23
14	174.93	0.6	0	1.0	—
15	174.93	0	0.5	1.0	3.83
16	174.93	0	0.75	1.0	17.53
17	174.93	0	1.0	1.0	> 22

EXAMPLE 2

Ultra fine cement compositions were prepared and tested for thickening time at various test temperatures from 140° F. to 400° F. The recipes of the compositions tested are set out in Table II-A. The test results are set out in Table II-B.

Some of the compositions included the acid form of the retarder (PBTC) and some included the salt form (SPBTC2). All of the compositions included one pound of dispersant per 100 pounds of dry cement.

It should be noted that all concentrations noted in Table II-A refer to the specific ingredient in undiluted (100% active) form even though the ingredient, for convenience, may have been added in diluted form.

It is further noted that the retarder salt (SPBTC2) referred to in Table II-A was prepared by neutralizing a 50 weight percent aqueous solution of PBTC with

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sodium hydroxide and diluting to a 25 weight percent aqueous solution having a pH of 2.4.

It is further noted that the compositions in Table II-A include "MICROSAND" silica flour. For test temperatures of less than 200° F. the concentration of "MICROSAND" silica flour was 40 pounds per 100 pounds of dry cement. For test temperatures greater than 200° F. the concentration of "MICROSAND" silica flour was 60 pounds per 100 pounds of dry cement.

The observations made with respect to the results shown in Table I are also to a substantial degree observed in Tables II-A and II-B.

TABLE II-A

Ultra Fine Cement Compositions and Thickening Times				
Composition	Water lb/100 lb dry cement	Retarder lb/100 lb dry cement		"Microsand" silica flour lb/100 lb dry cement
		PBTC	SPBTC2	
18	141.61	0.3	0	40
19	141.61	0.4	0	40
20	141.61	0.5	0	40
21	141.61	0.6	0	40
22	178.262	0.5	0	60
23	178.262	0.6	0	60
24	178.262	0.7	0	60
25	178.262	0.9	0	60
26	178.262	1.0	0	60
27	178.262	1.1	0	60
28	178.262	1.5	0	60
29	178.262	1.75	0	60

30	178.262	2.0	0	60
31	141.61	0.4	0	40
32	141.61	0.5	0	40
33	178.262	0.6	0	60
34	178.262	1.0	0	60
35	141.61	0	0.3	40
36	141.61	0	0.4	40
37	141.61	0	0.5	40
38	141.61	0	0.6	40
39	141.61	0	0.7	40
40	178.262	0	0.6	60
41	178.262	0	0.75	60
42	178.262	0	0.9	60
43	178.262	0	1.0	60
44	178.262	0	2.0	60
45	178.262	0	3.0	60
46	141.61	0	0.5	40
47	141.61	0	0.6	40
48	178.262	0	0.75	60

TABLE II-B

Composition	Thickening Times Ultra Fine Cement Compositions							
	Thickening Time, Hours							
	140° F.	160° F.	190° F.	220° F.	250° F.	300° F.	350° F.	400° F.
18	—	1.33	—	—	—	—	—	—
19	—	3.5	1.33	—	—	—	—	—
20	—	7.17	3.03	—	—	—	—	—
21	—	—	6.1	—	—	—	—	—
22	—	—	—	2.8	—	—	—	—
23	—	—	—	3.83	—	—	—	—
24	—	—	—	6.83	—	—	—	—
25	—	—	—	—	2.97	—	—	—
26	—	—	—	—	5.93	—	—	—
27	—	—	—	—	9.63	—	—	—
28	—	—	—	—	—	3.5	—	—
29	—	—	—	—	—	12.07	—	—
30	—	—	—	—	—	—	6.65	3.32
31	—	4.03	—	—	—	—	—	—
32	—	—	2.23	—	—	—	—	—
33	—	—	—	4.02	—	—	—	—
34	—	—	—	—	4.7	—	—	—
35	2.27	—	—	—	—	—	—	—
36	4.0	2.27	—	—	—	—	—	—
37	5.63	3.75	2.33	—	—	—	—	—
38	—	4.87	4.32	—	—	—	—	—
39	—	—	7.38	—	—	—	—	—
40	—	—	—	2.13	—	—	—	—
41	—	—	—	3.38	—	—	—	—
42	—	—	—	6.85	—	—	—	—
43	—	—	—	—	3.5	—	—	—
44	—	—	—	—	—	3.67	2.0	—
45	—	—	—	—	—	—	6.25	4.18
46	—	2.95	—	—	—	—	—	—
47	—	—	3.65	—	—	—	—	—
48	—	—	—	4.17	—	—	—	—

EXAMPLE 3

Selected compositions from Tables I and II-A were tested for compressive strength at various temperatures. The compositions tested and the test results are set out in Table III.

TABLE III

Composition	24 Hour Compressive Strength of Selected Ultra Fine Cement Compositions			
	Compressive Strength, lb/Sq. In.			
	187° F.	200° F.	250° F.	272° F.
4	—	580	—	—
10	225	—	—	213
14	197	—	—	215
37	—	836	—	—
38	—	795	1973	—
41	—	—	1742	—

EXAMPLE IV

Ultra fine cement compositions were prepared and tested for thickening time at various test temperatures from 140° F. to 300° F. The recipes of the compositions tested are set out in Table IV-A. The test results are set out in Table IV-B.

The compositions either contained a prior art retarder (MMCR) as previously described (49-64) or no retarder at all (65 and 66). All the compositions included both a dispersant and "MICROSAND" silica flour as described above with respect to Table II-A.

The compositions in Table IV-A and the results shown in Table IV-B are provided for comparison purposes only and are not examples of compositions of this invention.

TABLE IV-A

Composition	Ultra Fine Cement Compositions		
	Water lb/100 lb dry cement	Retarder lb/100 lb dry cement MMCR	"Microsand" silica flour lb/100 lb dry cement
49	99.96	0.17	40
50	99.96	0.26	40
51	99.96	0.35	40
52	99.96	0.44	40
53	141.61	0.1	40
54	141.61	0.2	40
55	141.61	0.3	40
56	141.61	0.4	40
57	141.61	0.5	40
58	141.61	0.6	40
59	178.262	0.75	60
60	178.262	1.0	60
61	178.262	2.0	60
62	141.61	0.3	40
63	141.61	0.4	40
64	178.262	0.75	60
65	141.61	0	40
66	178.262	0	60

TABLE IV-B

Composition	Thickening Times Ultra Fine Cement					
	Thickening Time, Hours					
	140° F.	160° F.	190° F.	220° F.	250° F.	300° F.
49	1.63	—	—	—	—	—
50	5.25	—	—	—	—	—
51	6.90	—	—	—	—	—
52	10.17	—	—	—	—	—
53	1.37	—	—	—	—	—
54	3.02	—	—	—	—	—
55	5.52	4.12*	—	—	—	—
56	11.37	6.98*	3.0*	—	—	—
57	—	—	6.62*	—	—	—

TABLE IV-B-continued

Composition	Thickening Times Ultra Fine Cement					
	Thickening Time, Hours					
	140° F.	160° F.	190° F.	220° F.	250° F.	300° F.
58	—	—	9.52*	—	—	—
59	—	—	—	7.9	—	—
60	—	—	—	—	4.8	—
61	—	—	—	—	—	5.43
62	7.10	—	—	—	—	—
63	—	4.02	4.22	—	—	—
64	—	—	—	10.53	—	—
65	—	0.68	—	—	—	—
66	—	—	—	0.72	—	—

*Slurry formed premature gel

What is claimed is:

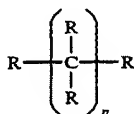
1. A method of cementing a subterranean zone penetrated by a wellbore at a temperature in the range of from about 40° F. to about 400° F. comprising the steps of:

pumping a set retarded ultra fine cement composition into said zone, said cement composition consisting essentially of,

an ultra fine hydraulic cement having a particle size no greater than about 30 microns and a Blaine Fineness no less than about 6000 square centimeters per gram.

sufficient water to form a pumpable slurry, and a set retarder comprised of a water soluble aliphatic compound containing at least three carbon atoms and at least one phosphonic acid or phosphonate group present in said slurry in an amount in the range from about 0.01 to about 5.0 pounds per 100 pounds of dry cement therein.

2. The method of claim 1 wherein said water soluble aliphatic compound is defined by the formula



wherein R is —H,



or —P(OX)₃, X is —H, Na or K and n is 3, 4, 5, or 6.

3. The method of claim 1 wherein said water soluble compound is selected from the group consisting of

2-phosphono-1,4 butane dicarboxylic acid,
2-phosphono-1,2 butane dicarboxylic acid,
2-phosphono-1,2,4 pentane tricarboxylic acid,
2-phosphono-1,2 pentane dicarboxylic acid,
2-phosphono-1,4 pentane dicarboxylic acid,
3-phosphono-1,5 pentane dicarboxylic acid and
3-phosphono-1,2 pentane dicarboxylic acid.

4. The method of claim 2 wherein said aliphatic compound has a pH in the range of less than about 1 to about 8.5.

5. The method of claim 4 wherein said aliphatic compound has a pH in the range of from about 2 to 7, X is —H or Na and said compound is present in said slurry in an amount in the range of from about 0.1 to about 2 pounds of dry cement.

6. The method of claim 2 wherein said aliphatic compound is selected from 1, 2, 4 butanetricarboxylic acid and the sodium salt thereof having a pH of about 2.4 and is present in said slurry in an amount in the range of from about 0.3 pound to about 1 pound per 100 pounds of dry cement.

7. The method of claim 6 wherein said cement composition is further characterized to include a dispersing agent comprised of a polymer prepared by the caustic-catalyzed condensation of formaldehyde with acetone or a substance derived from acetone wherein said polymer contains sodium sulfonate groups present in an amount in the range of from about 0.5% to about 2.0% by weight of dry cement therein.

8. The method of claim 7 wherein said cement composition is further characterized to include a fluid loss control agent comprised of a copolymer of N,N-dimethylacrylamide and 2-acrylamido, 2-methyl propane sulfonic acid present in an amount in the range of from about 0.5% to about 2.0% by weight of dry cement therein.

* * * * *

United States Patent [19]
Clarke

[11] **Patent Number:** 4,761,183
[45] **Date of Patent:** Aug. 2, 1988

- [54] **GROUTING COMPOSITION COMPRISING
SLAG**
- [75] **Inventor:** William J. Clarke, 162 Spencer Pl.,
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- [21] **Appl. No.:** 4,668
- [22] **Filed:** Jan. 20, 1987
- [51] **Int. Cl.⁴** C01B 7/14
- [52] **U.S. Cl.** 106/117; 52/744
- [58] **Field of Search** 106/117; 52/744

References Cited

U.S. PATENT DOCUMENTS

3,923,534	12/1975	Cassidy	106/85
4,054,460	10/1977	Buchet et al.	106/97
4,126,003	11/1978	Tomic	106/90
4,126,005	11/1978	Coursen	106/90
4,127,001	11/1978	Tomic	106/90
4,174,227	11/1979	Tomic	106/85
4,302,251	11/1981	Udagawa et al.	106/92
4,306,910	12/1981	Miyoshi	106/117
4,402,749	9/1983	Hall	106/76
4,415,364	11/1983	Naito	106/84
4,443,260	4/1984	Miyoshi	106/117
4,487,632	12/1984	Sherif et al.	106/85
4,505,752	3/1985	Sherif et al.	106/85
4,545,797	10/1985	Ecattar	106/117

FOREIGN PATENT DOCUMENTS

57-67051	4/1982	Japan	
57-164186	10/1982	Japan	
61-48470	3/1986	Japan	106/117

OTHER PUBLICATIONS

Concrete Manual, 8th ed., USDI, pp. 439-441 (1981).
"Ultra-Superfine Grout Material-Onoda MC", Onoda
Cement Co., 1-1-7, Toyosu, Koto-Ku, Tokyo, Japan,
Note "10-79 F. P.", at bottom of last page (28).
"Performance Characteristics of Microfine Cement",
by William J. Clarke, Preprint 84-023, Am. Soc. Civil
Engineers Convention, Atlanta, Ga., May 14, 1984.
"Ultra Fine Grouting Material", by M. Shimoda and H.
Ohmori, Proceedings of the Conference on Grouting in
Geotechnical Engineering, Feb. 10-12, 1982, ASCE.
"Ultrafine Cement Pressure Grouting to Control
Ground Water in Fractured Granite Rock", by D. W.
Moller et al, Paper SP83-8, American Concrete Insti-
tute, Kansas City, Sep. 29, 1983.

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[57]

ABSTRACT

A grouting composition, a method of grouting and a
formation so grouted are disclosed. The composition
comprises a very small particle size slag, an equal or
greater weight of water and the optional components
cement, alkali silicate, anionic dispersant, a source of
orthophosphate ions, sodium hydroxide and sodium
carbonate. The grout is particularly adapted to the
treatment of "tight" or low permeability formations
being low in viscosity and having controllable set time
and hardening time as well as high strength upon hard-
ening. Being based on slag, a byproduct, the grout is
economical.

17 Claims, No Drawings

GROUTING COMPOSITION COMPRISING SLAG

This invention provides an improved and economical grouting composition or grout, which is suitable for stabilizing and strengthening earthen formations, especially those employed in permanent structures such as buildings, tunnels and dams. The composition and the methods and procedures for its use are particularly suited to curtain grouting dams, sealing off underground streams, isolating of buried containers, reinforcing and protecting of building foundations, protecting of excavations, especially those used in the construction of subways, breakwater and bridge piers, and other applications for sealing or closing of passageways to the transport of fluids therethrough. The grouting composition of this invention is particularly fluid having an equal or greater weight of water than cementitious material.

Although relatively low in cost, the composition is surprisingly efficient, especially in a one component injection process. The composition has low viscosity, predictable set time, high ultimate strength and producing a sealed formation of very low permeability to fluids, particularly aqueous systems. This composition, comprising a suspension of cementitious solids, penetrates formations with a facility hitherto considered characteristic of solution grout compositions but develops the higher formation strength characteristic of the best suspension compositions.

Being free of organic chemicals except for a small amount of dispersant, by its nature substantive to the matter in the formation being grouted, the grout of this invention is non-polluting. This grout does not contribute to underground water or soil pollution in formations in which the grout is used. The non-polluting aspect of the grout is particularly important in environmental improvement applications. In these applications the very low permeability, to water and other fluids, of the grouted substrate is a most significant property resulting from the use of this invention. Examples of environmental improvement applications are the sealing of reservoirs for storage of waste materials, including toxic and radioactive wastes, and the sealing of formations where unwanted seepage into underground aquifers is occurring.

A major application of the grout of this invention is rehabilitation of structures such as buildings, bridges, dams and subways. A particularly important application is the regrouting of dam curtains, especially grouted curtains which have shown evidence of deterioration. Such deterioration is often evidenced by increased seepage and even eventual loss of dam core material.

The "one component" or single fluid grout of this invention does not have the difficulty controlled on site mixing and proportioning operations inherent in other types such as "two component" systems. The single fluid grout of this invention contain the necessary ingredients to produce the final high strength solidified state. The single fluid grout is programmed, by composition, to have a set time high enough to facilitate ease of injection into a formation to be grouted yet low enough to prevent its dilution or loss from the formation grouted.

However, in certain applications of this invention very fast set times, such as five to thirty minutes, are desired. These are readily achieved by two component grout compositions which employ the ultrafine cemen-

titious materials in one component and silicates in a second component.

In its various aspects this invention concerns: (1) a composition adapted for use in grouting, (2) a method of grouting comprising preparing the composition and injecting the composition into a formation and (3) a formation grouted by the composition.

The grouting composition of this invention comprises an ultrafine slag and water. The ultrafine slag is a cementitious material (CM) having a specific surface area greater than 9500, preferably greater than 11,000 and most preferably greater than 13,000 square centimeters per gram and, by weight, less than 3%, preferably less than 1.5% and most preferably no particles of the slag larger than 7.8 micrometers (μm) in diameter. (The surface area and particle size are measured by the use of the Microtrac $\text{\textcircled{R}}$ instrument further described hereinbelow.) An optional cementitious material in the composition is cement having a specific surface area greater than 7000, preferably greater than 8000 and most preferably greater than 9000 square centimeters per gram with, by weight, less than 16%, preferably less than 7% and most preferably less than 3% of particles of the cement larger than 7.8 micrometers in diameter as measured by the Microtrac $\text{\textcircled{R}}$ instrument. The preferred cement is portland cement.

The cementitious material is at least 40%, preferably 60%, more preferably 80% and most preferably 100% slag by weight.

The water to cementitious material weight ratio is 1:1 to 12:2, or greater preferably 1.5:1 to 7:1 and most preferably 2:1 to 3:1 i.e. there is always at least as much water as cementitious material and sufficient water to form a flowable grout.

For adapting to specific use requirements or operating conditions, additional materials in the grout are as follows, amounts being in weight percent solids based on the weight of cementitious material unless otherwise noted:

An effective amount of dispersant to disperse the cementitious material, preferably up to 2%, and most preferably 0.2% to 0.5%.

NaOH , Na_2CO_3 or a mixture of these, when employed, is greater than zero and up to about 15%, preferably up to 10% and most preferably about 3% to 8% of the weight of slag plus about 0% to 4% of the weight of cement.

An alkali silicate, when employed, is greater than zero and up to about 150%, preferably 30% to 75%.

When an alkali silicate is present, up to about 10%, preferably about 1% to 5% of orthophosphate ion is also provided.

Other optional ingredients comprise materials such as inert filler material as discussed hereinbelow.

In certain applications combinations of slag and cement have the most appropriate properties, in others, alkali silicate is desired as a third large component of the composition, in still others, slag and silicate give the desired properties. One of the advantages of this invention is the ease with which the composition can be altered to adapt to set time, strength, ultimate permeability of the grouted formation and other requirements for the specific job. Combinations of portland cement and slag in the composition furnish grouts having an outstanding combination of permeation, set time and strength; even modest amounts of cement in such compositions produce grout having a controllable desirable set time. Combinations of these ingredients lead to opti-

mum strength, particularly unconfined compressive strength.

The slag employed in this invention is a by-product obtained in the blast furnace process of smelting iron ore to produce iron. The slag is produced by a conventional process, outlined below, utilizing grinding and separating steps well known in the art. In the blast furnace, slag is generated, typically at about 1550° to 1650° C., from other minerals in the iron ore, coke ash and the limestone used as a flux. This slag is skimmed from above the iron, granulated by treatment with water and ground. Typically the granulation employs high pressure water sprays followed by immersion of the slag in a pit of water to produce a slag having a high glass content. However produced, it is desired that the slag used in this invention have a high glass content, preferably above about 95% glass. It is also preferred that the water content be low, preferably below about 15%. Typical dry composition range and two examples of slag are (in weight percent):

Com-position	SiO ₂	Al ₂ O ₃	CaO	MgO	FeO	S	Mn ₂ O ₃
Usual Range	30-40	8-18	35-50	0-15	0-1	0-2	0-2
Typical	36.4	16.0	43.3	3.5	0.3	0.5	<0.1
Typical	35.5	11.4	39.4	11.9	0.2	0.2	—

The slag used in this invention has a specific surface area over 9500 cm²/gm, desirably over 11000 cm²/gm and most preferably over 13000 cm²/gm.

The high glass content, finely divided slag yields a grout having excellent sulfate resistance and readily controlled setting and hardening times in a relatively inexpensive formulation. High sulfate resistance is particularly important with regard to long term stability of the grouted formation. Grout failures after five or ten years have been attributed to sulfate attack. The slag-rich compositions of the present invention have long term stability in formation and are also useful in regrouting formations in which a previous grout has exhibited signs of failure. The grout is particularly inexpensive because of the comparatively low cost of slag, a byproduct of iron production.

High level of penetration into a tight formation associated with high permanence renders the instant composition valuable in many applications. One example is in radioactive waste storage in shafts deep in rock formations where the instant grout composition is employed to permeate the rock around the waste containers and thus furnish a secondary barrier to both intrusion of ground water and leaking of waste from the containers.

Portland cement is a hydraulic cement consisting mainly of calcined silicates of calcium. Five types of portland cement (I through V) are generally recognized, their manufacture, properties and characteristics are described in detail by J. F. Young, ACI (American Concrete Institute, Detroit, Mich.) Education Bulletin No. E3-83, pages 1 through 8, herein incorporated by reference.

It is a novel feature of this invention that cementitious material having the fine particle size and distribution described is formulated in a composition producing a high strength grout having a readily controlled set time.

While portland cement and/or slag are preferably used without inert filler material, in some instances it may be desirable to incorporate limited amounts of

other solids meeting the particle size specifications specified for slag hereinabove. Such other solids are clay, bentonite, kaolin, vermiculite, limestone, silica flour, silica fume and other well known inert solids. The amount of these employed is to be minor so as not to reduce the strength of the set grout below desired values such as those in the examples of this invention hereinbelow.

The alkali silicate is preferably an aqueous colloidal suspension of an alkali salt of silicic acid. Throughout the specifications and claims, the term "alkali silicate" is intended to refer to alkali metal silicates having an alkali metal oxide:silicon dioxide weight ratio within the range of from about 1.0:3.0 to 1.0:4.0, notably sodium silicates having a sodium oxide:silicon dioxide weight ratio within the range of from about 1:3.0 to 1:4.0, preferably, about 1:3.0 to 1:3.5. An especially preferred material is an aqueous sodium silicate having a sodium oxide:silicon dioxide ratio of about 1:3.2 to 1:3.3 and a Na₂O:SiO₂ solids content of about 35 to 45%. The term "alkali metal", as used in the specification and claims is intended to refer to the various alkali metals, i.e., sodium, potassium, lithium, rubidium, cesium and mixtures thereof. Silicates of potassium and sodium are more generally available. Because of their lower cost and availability, sodium silicates are more widely used and therefore are preferred in the practice of the present invention. Particular reference hereinafter is made to such silicates. The alkali silicate is especially useful in the preparation of low cost compositions having a very fast set time for uses such as underground water control.

The dispersant is selected from the well-known group of materials used to disperse solids, preferably water-wettable solids, in aqueous systems. The dispersant serves to aid the penetration of water into the finely divided solids to produce a suspension of unassociated or unagglomerated particles. These dispersants are generally negatively charged or anionic electrolytes especially polyelectrolytes, such as polycarboxylates and polysulphonates. Examples include sodium or ammonium salts of polymethacrylic acid, diisobutylene-maleic anhydride copolymer, copolymers of acrylic, methacrylic and maleic acids, organic phosphates, sulfonated naphthalene formaldehyde condensates, sulfonated natural products and other sulfonated polymer condensates.

The orthophosphate ion is any of the orthophosphate ions generally existing in equilibrium with each other in aqueous solution, PO₄⁻⁻⁻, HPO₄⁻⁻ and H₂PO₄⁻. In highly alkaline systems it is expected that PO₄⁻⁻⁻ predominates. Two of the most available sources of orthophosphate ion are orthophosphoric acid, H₃PO₄ and sodium phosphate decahydrate, Na₃PO₄·10H₂O. Phosphoric acid is commonly the commercial grade 85%, by volume, with water. Other phosphates such as the polyorthophosphates, may be employed as the source of the orthophosphate ion. The orthophosphate ion is useful in control of the set time, especially in grout compositions comprising alkali silicates, by delaying setting.

The NaOH is commercially available in solid and aqueous solution grades, the Na₂CO₃ is usually a solid grade, each serves to control the rate of hardening of the composition, particularly in formulations high in slag. Thus, NaOH and/or Na₂CO₃ may be regarded as a set time catalyst which has little if any effect on other properties of the grout, however overdosage will de-

crease strength. Favored are formulations in which the Na_2CO_3 is less than equal to NaOH by weight.

The importance of controlled rapid set time is seen, for example, in dam curtain rehabilitation. In a typical case water is moving through the curtain, at perhaps one or two feet per hour, and the grout injection holes in the dam curtain are on ten foot centers. Thus the set time of the grout must be less than five hours, preferably in the half hour to five hour range and must be predictable. This invention teaches predictability in both set time and permeation, particularly in tight formations previously grouted where degraded cement results in increased seepage. The ultrafine slag permeates the degraded cement, hardens and reduces seepage of the rehabilitated dam grout curtain.

In general, portland cement contributes to decreasing the set time and increasing the strength of a formulation. Slag, without cement has longer set times but this is controlled by the use of NaOH and Na_2CO_3 . Higher than optimum levels of NaOH and Na_2CO_3 tend to decrease the final strength and increase the cost of the formulation. When alkali silicate is employed, optimization of the slag-cement-silicate ratios can result in a formulation with too fast a set. This low set time can then be increased, with little effect on strength, by the addition of phosphate ions. In all formulations the viscosity of the grout is readily controlled by the amount of water present. Thus in each case the invention teaches the balancing of the composition variables needed to give the optimum grout for the given application.

Another novel feature of this invention is based on the finding that NaOH and Na_2CO_3 are unexpectedly efficient and effective in controlling the set time of mixtures of slag and alkali silicate. When cement is used to control the set time of admixtures with slag and silicate there is the difficulty of mixing the appropriate ratio of the three large components in the field and a second difficulty is that flocculation of the system occur before setting. The latter leads to poor permeation of the formation being grouted. The use of NaOH , Na_2CO_3 or a mixture of these speed the set time to a suitable range, employing a small amount which is easily measured and added in the field, and additionally produces no separation or flocculation in the grout before setting. Finer control of the set time can be obtained by the addition of phosphate ion as in other alkali silicate systems, if desired.

Without being bound by theory, offered as a pedagogical aid in teaching the invention, it is clear that since the slag is essentially free of available calcium ion the formation of calcium silicate does not occur. The formation of the calcium salt is likely to be responsible for the separation or flocculation observed when cement is present. The lack of exchangeable calcium in slag is also thought to contribute to the effectiveness of the NaOH and Na_2CO_3 in acceleration of the setting of silicate-slag systems.

The following examples will further illustrate the invention but are not intended to limit it in any way. All parts and percentages are by weight and all temperatures in degrees Centigrade unless otherwise noted.

Particle Size of Cementitious Materials

The particle size of the materials is determined by a laser light scattering particle size distribution apparatus identified as a Microtrac® particle size analyzer (Leeds and Northrup Instruments, North Wales, Pa.

19454). Measurements are made in the 0.7 to 125 micron (μm) range and are presented in terms of the volume of particles in size channels having a size ratio of approximately 1.4 between channels. Table I. presents results of the average of three runs given as the percent larger than the stated size for each channel limit and the calculated volume surface area of the sample in square meters per cubic centimeter. The volume surface area can be converted to the specific surface, in square meters per gram, by dividing by the density of the material. Portland cement density is considered 3.15 grams per cubic centimeter as in ANSI/ASTM standard C 204-78a; slag density is considered 2.92 grams per cubic centimeter.

The procedure for analyzing slag samples in the Microtrac® is as follows: Two grams of slag are dispersed in reagent grade alcohol (denatured ethanol) until the equilibrium uncalibrated sample volume (dV) is reached without the presence of air bubbles. Each sample is analyzed in three 30 second runs, the results are then averaged.

The particle size data resulting from a triplicate set of Microtrac® measurements are a table of volume percent of sample larger than a given size, diameter, in micrometers. The Microtrac® instrument also furnishes the following summary data, employing these abbreviations:

dV: Uncalibrated Sample Volume

%10: Microns at 10th percentile

%50: Microns at 50th percentile

%90: Microns at 90th percentile

MV: Volume Mean Diameter

CS: Calculated Surface Area (m^2/cc)

STD. DEV.: Standard Deviation

Ma: Area Mean Diameter

Table I presents the particle size data for typical examples of the slag of this invention (M1) and the cement of this invention (M3). In table II is a summary of the particle size data obtained on a number of samples.

Particle Size Distribution, Table I.

Channel Upper Limit (μm)	Percent Larger Than	
	Sample M1	Sample M3
31	0.0	0.0
22	0.0	1.1
16	0.0	3.9
11	0.0	7.4
7.8	1.5	14.9
5.5	8.4	27.6
3.9	19.4	42.8
2.8	34.1	57.0
1.9	53.9	72.6
1.4	76.0	87.8
0.9	92.9	97.8
0.7	100.0	100.0

Summary of Microtrac Data, Table II.

Sample	Code	% Coarser than 11 μm	% Coarser than 7.8 μm	CS	cm^2/gm
M1	4/17	0.0	1.8	3.901	13200
M1	5/8	0.0	0.8	4.035	13900
M1	5/8	0.0	0.9	3.710	12700
M1	8/15	0.0	1.5	3.176	10900
M1	8/15	0.0	1.8	3.065	10500
M1	12/5	0.0	0.0	4.391	15100
M1	12/5	0.0	0.2	3.981	13600

-continued

Summary of Microtrac Data, Table II.					
Sample	Code	% Coarser than 11 μ m	% Coarser than 7.8 μ m	CS	cm ² /gm
M1	12/5	0.0	0.4	3.856	13200
M3	5/8	7.4	14.9	2.263	7180
M3	5/8	7.5	14.7	2.321	7370
M5	4/17	2.3	10.9	2.570	8480
M5	5/8	1.3	7.5	2.876	9490
FS	4/17	2.3	8.6	2.572	8810
FS	8/15	2.0	5.5	2.886	9880
FS	8/15	1.4	4.4	2.762	9460
OS	8/15	27.7	39.8	1.683	5760
OP I	12/29	50.3	59.5	1.219	3870
OP III	12/29	40.0	49.2	1.667	5290

Symbols used in tables and examples:

M1 = ultrafine slag of this invention

M3 = ultrafine cement

M5 = ultrafine commercial slag/cement (80/20)

FS = fine slag

OS = ordinary slag

OP I = type I portland

OP III = type III portland

Set Time

Set time and Other Physical Measurements are determined by the following procedure, employing the formulations given in the tables.

1. Water is added to a plastic cup
2. NaOH and Na₂CO₃ are added as required and dissolved.
3. Dispersant is added and dissolved.
4. Cementitious material is added and agitated for 10 seconds by a high speed mixer.
5. The cup is tilted periodically while the CM surface is observed. When there is no flow or gross motion of the CM surface while the cup is tilted to 45 degrees the time is noted; this is the set time.

Other observations are also made on the sample. A

some formulations this is a quick indication of hardening. Particularly at high water ratios, settling of the CM is observed; the percent of the total volume present as clear surface liquid is reported as percent settlement.

- 5 Hardness development is monitored by measurement of the compressive strength and is reported along with the time after sample preparation. The strength measurement employs a handheld penetrometer (Soiltest CL-700 Pocket Penetrometer, Soiltest Inc., Chicago, Ill.)
- 10 and follows the manufacturers instructions. The penetrometer is held by its handle with the piston at right angles to the CM surface. With steady pressure the piston is pushed into the CM to the depth of the calibration groove about $\frac{1}{4}$ inch from the end of the piston.
- 15 compressive strength is read on the scale of the instrument.

Examples 1 and 2 show the effects of water ratio, NaOH content and Na₂CO₃ content on the set time and other properties. It is seen that formulations with NaOH have lower viscosities than those with Na₂CO₃, thus promote ease of permeation by the grout, but have higher set times.

- 25 M1, M3 and M5 are as defined in Summary of Microtrac Data, Table II above. N2 is the dispersant, at 43% solids aqueous, sodium naphthalene sulfonate formaldehyde polymer (CAS No. 9084-06-4). When present sodium silicate (SiO₂/Na₂O=3.22; employed as 37.8% aqueous) is further diluted with the second water charge to make the second component of a two component system. The two components are then mixed and the timing started. H₃PO₄, orthophosphoric acid, is 85% acid (aqueous).
- 30
- 35

EXAMPLE 1

Accelerators

1:1 Water/CM Ratio

	A	B	C	D	E	F	G	H	I
Formulation									
Water (gms)	50	50	50	50	50	50	50	50	50
NaOH (gms)	1	2	4				0.5	1	2
Na ₂ CO ₃ (gms)				1	2	4	0.5	1	2
N2 (43%) (gms)	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
M1 (gms)	50	50	50	50	50	50	50	50	50
Results									
Viscosity	low	low	low	med	med	high	low	low	med
minutes	15	13	12	10	9	7	6	5	5
Set time (hr)	24	8	4.8	4.7	1.7	0.6	9	4.7	1.2
kg/cm ² (1)	>4.5	>4.5	>4.5	0.25	>4.5	>4.5	>4.5	>4.5	3.0
hours	33	21	21	21	21	21	21	21	4.7
kg/cm ² (1)				>4.5					>4.5
hours				34					7.8
Color	lb	lb	lb	lb	lb	mb	lb	mb	mb
hours	46	21	21	21	21	21	21	21	4.7

(1) Unconfined Compressive Strength

lb light blue

mb medium blue

qualitative estimate of the viscosity is made after the gross air entrained by the agitation has left but well before the sample has set. Estimated viscosities are: medium—approximates mid-range motor oil, high—approximates glycerine, low—water viscosity; all at room temperature. The color of the sample is observed; in

EXAMPLE 2

Accelerators

2:1 Water/CM Ratio

	A	B	C	D	E	F	G	H	I
Formulation									
Water (gms)	100	100	100	100	100	100	100	100	100
NaOH (gms)	2	4	6				1	2	3
Na ₂ CO ₃ (gms)				2	4	6	1	2	3

-continued

	A	B	C	D	E	F	G	H	I
N2 (43%) (gms)	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
M1 (gms)	50	50	50	50	50	50	50	50	50
Results									
Viscosity	low	low	low	med	med	high	low	med	high
hours	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4
Settlement (%)	50	50	30	20	20	20	30	20	10
Set time (hr)	8	6	4	8	6	4.5	9	4.5	2.1
kg/cm ² (1)	0.5	2.0	2.3	soft	soft	0.5	4.0	0.25	4.0
hours	18	14	14	20	20	18	14	7.5	7.5
kg/cm ² (1)	2.3	3.7	3.7	>4.5	>4.5	>4.5	>4.5	>4.5	>4.5
hours	20	20	20	33	33	20	20	10	10
kg/cm ² (1)	>4.5	>4.5	>4.5						
hours	72	72	72						
Color	mb	lb	lb	lb	lb	lb	lb	lb	lb
hours	72	14	14	33	33	18	14	10	10

(1)Unconfined Compressive Strength

Color Code

mb medium blue

lb light blue

EXAMPLE 3

Comparison of Set Times for M1, M3, and M5

	A	B	C	D	E	F	G	H
Formulation								
Water (grams)	50	50	50	50	100	100	100	100
N2 (43% solids)	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
M1 (grams)	50			40	50			40
M3 (grams)		50		10		50		10
M5 (grams)			50				50	
Results								
Viscosity	low	high	low	low	low	med	med	low
minutes	15	10	8	5	60	55	50	45
Settlement (%)	15	10	5	5	10	15	20	15
minutes	93	75	67	67	55	50	41	36
Set time (hrs)	—	0.8	1.3	0.8	3.3	2.7	1.7	8.3
kg/cm ² (1)	soft	0.7	4.0	3.5	soft	4.0	0.3	0.3
hours	23	9	23	23	46	23	22	22
kg/cm ² (1)	1.3	3.0	>4.5	>4.5	>4.5	>4.5	>4.5	>4.5
hours	48	12	48	46	129	46	45	46
kg/cm ² (1)	>4.5	>4.5						
hours	94	23						
Color	w	dg	db	db	w	dg	db	b
hours	94	96	96	96	47	46	45	45

(1)Unconfined Compressive Strength

Color Code:

w = white

dg = dark gray

db = dark blue

b = blue

EXAMPLE 4

Set Time of Silicate/CM

	A	B	C	D	E	F	G	H	I
Formulation									
Water (gms)	50	50	60	60	60	60	60	60	60
N2 (43%) (gms)	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
M1 (gms)	50		18	16	20			10	15
M3 (gms)			2	4		20		10	5
M5 (gms)		50					20		
Water (gms)			40	40	40	40	40	40	40
Silicate SiO ₂ /Na ₂ O(3.22, 37.8%) (gms)			38	38	38	38	38	38	38
Results									
Set time (min)	22 hr	8 hr	20	6	6 hr	0.5	1.7	2	3
Settlement (%)	10	20	0	0	50	0	0	0	0
hours	14	14			34				
kg/cm ² (1)	soft	soft	soft	soft	soft	0.75	0.7	1.0	0.2
hours	14	14	45	8	34	1	8	4	4
kg/cm ² (1)	>4.5	>4.5	soft	0.8	soft	3	1.2	1.8	1.3
hours	82	82	94	70	93	4	22	19	19
kg/cm ² (1)			soft	>4.5	soft	>4.5	>4.5	>4.5	>4.5
hours			183	172	183	20	70	82	82
Color	w	b	w	g	w	g	g	g	g

-continued

	A	B	C	D	E	F	G	H	I
hours	82	82	94	70	93	20	22	34	34

(1)Unconfined Compressive Strength

Color Code:

w = white

b = blue

g = gray

EXAMPLE 5

10

Permeation Test Procedure

Set Time of Silicate/CM

1. Press a rubber stopper into an end of the glass cylin-

	A	B	C	D	E	F	G	H	I
Formulation									
Water (gms)	50	50	50	50	50	50	60	60	60
N2 (43%) (gms)	0.5	0.5	0.3	0.3	0.5	0.5	0.2	0.2	0.2
NaOH (gms)	2		0.5		1.0		0.8		
Na ₂ CO ₃ (gms)		2		0.5		1.0			
M1 (gms)	50	50	25	25	50	50	20		
M5 (gms)								20	
M3 (gms)									20
water (gms)	40	40	20	20	40	40	40	40	40
H ₃ PO ₄ (85%) (gms)								0.4	0.4
Silicate as in Ex. 4 (gms)	38	38	19	19	38	38	38	38	38
Results									
Viscosity	med	high	low	low	low	med	low	low	low
Set Time (hr)	0.15	0.25	0.7	1.5	0.33	0.5	4.7	0.16	0.03
kg/cm ² (1)	0.3	s	s	s	s	vs	vs	0.1	0.2
hours	0.66	15	15	15	15	14	18	4	0.5
kg/cm ² (1)	1.5	s	s	s	1.2	vs		0.2	0.5
hours	16	40	24	24	24	24	18	4	
kg/cm ² (1)	4.5		s	s	s	vs			0.7
hours	24		39	39	39	38		17	

(1)Unconfined Compressive Strength

Qualitative hardness code:

s = soft

vs = very soft

EXAMPLE 6

Permeation Test

The apparatus consists of:

- (1) a cell filled with fine sand, closed at each end by 45 a stopper having a single central hole,
- (2) a pressurized grout supply tank connected to the bottom of the cell by tubing and
- (3) a delivering system consisting of a tube, connected to the top of the cell, leading to a graduated cylinder collector vessel. The cell is a 5 cm I.D., 15 cm long glass cylinder having a sand-retaining assembly at each end.

Each assembly consists of:

- (1) a 70 mesh per inch polyester sieve cloth for retaining the sand, 55
- (2) a close-fitting ca 5 cm O.D. flanged disk with 12 holes 1/16 inch in diameter therethru,
- (3) a rubber stopper to seal the cylinder and to bear on the flange of the disk thereby creating a small plenum chamber between the disk and the stopper and 60
- (4) a metal end plate having a central hole to accommodate the tube passing therethru and edge-holes to accommodate threaded rods. Wing nuts on the threaded rods tighten down on the end plates thus forming a frame which clamps the assembly together so it can be pressurized without leaking. 65

der and then put a perforated disk and a sieve cloth into the tube.

2. Weigh enough Evanston beach sand for one sample.
3. Pour one third of the sand into the glass cylinder.
4. Place a solid metal cylinder as a weight (about 320 grams) on the top of the sand, and apply a vibrator in the sand or against the glass.
5. Repeat steps 3 and 4 twice; then place a sieve cloth and a perforated disk on the top of the sand.
6. Press a rubber stopper on the other end of the tube and assemble the frame.
7. Connect the supply and delivery tubes and apply pressure to water which is in the tank in order to saturate the sample.
8. Disconnect the tube connected to the bottom of the sample and let the water drain out by gravity. Record the volume of the water drained from the tube and label it as V1. This is the void volume in the sample before the injection of grout.
9. Prepare the grout and pour it into the tank emptied.
10. Apply 2 psi air pressure to the tank and collect the effluent from the top of the sample. Time the accumulated volumes of effluent and label them as V2, V3 etc.
11. The volume of slurry permeating the sample is V1 plus V2, V3, or V4 respectively.

Permeation Test Results

Formulation	A	B	C	D	E	F	G	H
CM	M1	M5	M1	FS	OS	M1	M1	M1
Water:CM	1:1	2:1	2:1	2:1	2:1	2:1	2:1	2:1

-continued

Formulation	A	B	C	D	E	F	G	H
Dispersant	N2	N2	N2	N2	N2	N2	HSR	HSR
% solids	0.43	0.43	0.43	0.43	0.43	0.43	0.6	0.02
on CM								
Sand Wt (g)	337	355	332	336	326	336	356	344
Sand Ht (cm)	9.7	10.1	9.0	9.8	9.7	9.9	10.4	10.1
Sand d.	1.68	1.7	1.78	1.66	1.62	1.64	1.65	1.64
(g/cc)								
V1 (cc)	13	13	14	11	13	12	14	13
V2 + V1	55	51	99	62	30	112	92	60
(cc)								
minutes	1	1	1	1	1	1	1	1
V3 + V1	81	101	204	93	38	249	162	65*
(cc)								
minutes	5	5	5	5	5	10	10	5*
V4 + V1	89*	123	326	122	62			
(cc)								
minutes	10*	12	20	20	20			

*flow stopped

The test results showed the differences in permeation among the grouts consisting of two parts water to one part cementitious material, by weight, employing the N2 dispersant at 0.43% solids on cement. Data are also furnished (1) at a 1:1 ratio with water and (2) employing another dispersant, Lubricon HSR (American Admixtures, Inc., Chicago, IL 60646) a salt of Hydroxylated carboxylic acids.

EXAMPLE 7

Permeability of Grouted Formation

A confined column of Evanston beach sand is grouted with each of the following grout formulations in parts by weight:

	A	B	C
M1	100	100	100
N2 solids basis	0.4	0.4	0.4
NaOH	1	5	10
Water	200	200	200

The permeability of the sand after the grout is hardened is very low being in the range 10^{-7} to 10^{-8} centimeters per second.

The Evanston beach sand is a fine sand having the following particle size distribution.

US Standard Sieve:	40	50	70	100	200
Wt. percent finer:	99	91	36	4	1

I claim:

1. A fluid composition for grouting comprising: (1) slag as a first cementitious material, the slag having a specific surface area greater than 9,500 square centimeters per gram and less than three weight percent of particles of the slag being larger than 7.8 micrometers in diameter and (2) an equal or greater weight of water.

2. The composition of claim 1 additionally comprising an effective amount of dispersant, to disperse the particles of slag, and the composition comprising up to 12 parts water per part slag, by weight.

3. The composition of claim 1 additionally comprising up to 15% NaOH, Na_2CO_3 or a mixture thereof based on the dry weight of the slag, and the slag having a specific surface area greater than 11,000 square centimeters per gram and less than 1.5%, by weight, of parti-

cles of the slag being larger than 7.8 micrometers in diameter.

4. The composition of claim 3 consisting essentially of one part slag and, based on the weight of the slag, 1.5 to 7 parts water, up to about 2% dispersant, and up to about 10% NaOH, Na_2CO_3 or a mixture thereof.

5. The composition of claim 4, the slag having a specific surface area greater than 13,000 square centimeters per gram with no particles of the slag being over 7.8 micrometers in diameter and, based on the weight of slag, about 2 to 3 parts water, about 0.2% to 0.5% dispersant and about 3% to 8% NaOH, Na_2CO_3 or a mixture thereof.

6. The composition of claim 1 additionally comprising a cement as a second cementitious material, the cement having a specific surface area greater than 7,000 square centimeters per gram and less than 16 weight percent of particles of the cement being larger than 7.8 micrometers in diameter, the slag being at least 40% of the total cementitious material by weight; the composition comprising up to 12 parts by water per part cementitious material by weight and an effective amount of a dispersant to disperse the cementitious material.

7. The composition of claim 6, the slag having a specific surface area greater than 11,000 square centimeters per gram with less than 1.5% by weight of particles of the slag being larger than 7.8 micrometers in diameter, the cement having a specific surface area greater than 8000 square centimeters per gram and less than 7% by weight of particles of the cement being larger than 7.8 micrometers in diameter, the slag being at least 60% of the cementitious material by weight, and additionally comprising NaOH, Na_2CO_3 or a mixture of these being up to 15% of the slag plus up to 4% of the cement by weight.

8. The composition of claim 7 comprising, per part cementitious material by weight, from 1.5 to 7 parts of water and up to 2% dispersant.

9. The composition of claim 8 consisting essentially of: slag having a specific surface area greater than 13,000 square centimeters per gram and no particles of the slag being larger than 7.8 micrometers in diameter; cement having a specific surface area greater than 9000 square centimeters per gram and less than 3% by weight of particles of the cement being larger than 7.8 micrometers in diameter; the slag being at least 75% by weight of the cementitious material; two to three parts of water per part of cementitious material by weight; 0.2% to 0.5% dispersant by weight based on the cementitious material; and Na_2CO_3 , NaOH or a mixture of these being 3% to 8% of the slag plus zero to 2% of the cement by weight.

10. The composition of claim 2 additionally comprising greater than zero and up to 150% alkali silicate based on the weight of slag.

11. The composition of claim 10, the slag having a specific surface area greater than 11,000 square centimeters per gram and less than 1.5%, by weight, of particles of the slag being larger than 7.8 micrometers in diameter and, based on the weight of the slag, up to 2% dispersant and up to 10% orthophosphate ion.

12. The composition of claim 11 consisting essentially of slag having a specific surface area greater than 13,000 square centimeters per gram and no particles of the slag being larger than 7.8 micrometers in diameter; 1.5 to 7 parts of water per part of slag by weight; and, based on the weight of slag, 30 to 75% alkali silicate, 0.2% to 0.5% dispersant and 1 to 5% orthophosphate ion.

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13. The composition of claim 10 additionally comprising a cement as a second cementitious material, the cement having a specific surface area greater than 7,000 square centimeters per gram and less than 16 weight percent of particles of the cement being larger than 7.8 micrometers in diameter, the slag being at least 40% of the cementitious material by weight.

14. The composition of claim 13 comprising: slag having a specific surface area greater than 11,000 square centimeters per gram and less than 1.5% of particles of the slag being larger than 7.8 micrometers in diameter, cement having a specific surface area greater than 8000 square centimeters per gram and less than 7% of particles of the cement being larger than 7.8 micrometers in diameter, and, based on the weight of cementitious material, up to 2% dispersant and up to 10% orthophosphate ion.

15. The composition of claim 14 consisting essentially of: slag having a specific surface area greater than

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13,000 square centimeters per gram and no particles of the slag being larger than 7.8 micrometers in diameter; cement having a specific surface area greater than 9000 square centimeters per gram and less than 3% by weight of particles of the cement being larger than 7.8 micrometers in diameter; the slag being at least 75% by weight of the cementitious material; 1.5 to 7 parts of water per part of cementitious material by weight; and based on the weight of cementitious material, 30 to 75% alkali silicate, 0.2 to 0.5% dispersant and 1 to 5% orthophosphate ion.

16. The composition of claim 11 additionally comprising NaOH, Na_2CO_3 or a mixture of these, being greater than zero and up to 10% of the slag by weight.

17. The composition of claim 14 additionally comprising NaOH, Na_2CO_3 or a mixture of these, being greater than zero and up to 10% of the slag by weight.

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UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 4,761,183

DATED : Aug. 2, 1988

INVENTOR(S) : William J. Clarke

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Column 1, line 11, cancel "of".

Column 1, line 12, cancel "of".

Column 1, line 13, cancel "of".

Column 1, line 29, after "compositions but" insert -- it--.

Column 1, line 30, cancel "higher" and insert -- high--.

Column 1, line 59, cancel "contain" and insert -- contains--.

Column 2, line 31, cancel "12:2" and insert -- 12:1--.

Column 6, line 36, cancel "Ma" and insert --MA--.

Column 7, line 22, cancel "Set Time" and insert --Set Time and Other Physical Measurements--.

Column 7, line 23 cancel the entire line starting "Set ..." and insert --Set time is deter---.

Column 8, Example 1, in the table footnotes below the line "(1) Unconfined Compressive Strength" insert --color code--.

Column 12, line 56, cancel "tank emptied" and insert --emptied tank--.

Column 13, line 64, (Claim 3, first line) cancel "claim 1" and insert --claim 2--.

Signed and Sealed this
First Day of August, 1989

Attest:

DONALD J. QUIGG

Attesting Officer

Commissioner of Patents and Trademarks

UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 4,761,183

DATED : Aug. 2, 1988

INVENTOR(S) : William J. Clarke

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Column 14, claim 6, line 8, cancel "by" and insert --of--.

Signed and Sealed this
Sixteenth Day of July, 1991

Attest:

Attesting Officer

HARRY F. MANBECK, JR.

Commissioner of Patents and Trademarks